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Microwave Spectrum, Quadrupolar Coupling Constants, and Dipole Moment of Chlorobenzene

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This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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Microwave Spectrum, Quadrupolar Coupling Constants, and Dipole Moment of Chlorobenzene*

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The microwave spectrum of chlorobenzene has been observed in the frequency range between 8000 and 30 000 Mc/sec. An analysis of this spectrum gives the following values for the rotational constants for the two isotopic species, $C_6H_5Cl^{35}$ and $C_6H_5Cl^{37}$; $A=5672.951$ Mc/sec, $B=1576.774$ Mc/sec, $C=1233.672$ Mc/sec for the Cl^{35} isotopic species and $A=5672.530$ Mc/sec, $B=1532.790$ Mc/sec, $C=1206.571$ Mc/sec for the Cl^{37} isotopic species. The quadrupolar coupling constants which were obtained from the quadrupolar hyperfine structure are $eqQ=-71.10$ Mc/sec for Cl^{35} and $eqQ=-56.10$ Mc/sec for the Cl^{37}. The quadrupolar asymmetry parameter η cannot be determined from the microwave spectrum. The observed dipole moment is 1.78 ± 0.06 D.

1. INTRODUCTION

THE microwave spectrum of chlorobenzene has been studied by Erlandsson[1,2] and Selen.[3] Erlandsson[1] obtained an assignment with rather crude measurements which he later[2] partially refined for chlorobenzene (Cl^{35}). The quadrupole hyperfine structure was not resolved in either of these studies. In addition, the assignment for the Cl^{37} isotopic species was left in a tentative state.[2] Somewhat later Selen[3] analyzed the partially resolved quadrupolar hyperfine structure for chlorobenzene (Cl^{35}) from which he obtained a value of -66.4 ± 8 Mc/sec for eqQ of Cl^{35}. This eqQ is inconsistent with the value obtained by Livingston[4] for the solid state. Selen made no attempt to evaluate eqQ for Cl^{37}.

Nuclear quadrupole spectroscopy has been used to measure the chlorine nuclear quadrupole coupling constants in the mono and dichlorobenzenes in the solid state.[4,5] The corresponding measurement of the gas-phase chlorine nuclear quadrupole coupling constant for mono chlorobenzene should and does correlate with the solid-state measurements.

Two other substituted benzenes, fluorobenzene,[6–9] and benzonitrile[10,11] have been studied recently. A complete ring structure has been obtained for benzonitrile,[11] while only a partial structure has been given for fluorobenzene.[9] The purposes of the present study were to carefully remeasure the chlorobenzene spectrum, to evaluate the nuclear quadrupole coupling constants for both chlorine isotopes, to determine the chlorobenzene dipole moment, and to provide at least a tentative structure of chlorobenzene suitable for comparison with the structures of the other substituted benzenes which have been studied.

A complete structure of chlorobenzene cannot be obtained here because only two isotopic molecular species have been examined. However, it is possible to obtain an estimate of the C–Cl distance by either assuming a regular hexagonal ring or by making use of the recent work of Bak *et al.*[11] in which the complete ring structure of a benzene derivative has been determined.

2. EXPERIMENTAL

A standard 100-kc/sec Stark modulation spectrometer[12] has been used for most of this study. The square-wave generator used for Stark modulation is a modification of the one described by Hedrick.[13] It provides 0.1 μsec rise and fall times at all square-wave voltages up to 2000 V. A phase stabilized microwave oscillator has been incorporated in the spectrometer for use in high-resolution studies.[14] Microwave frequencies were measured by interpolation receiver techniques for routine work and by methods described elsewhere[14] for high-resolution work. An HP 104 AR quartz oscillator with a rated stability of ±3 cycles in 10^{10} cycles/day and 5 cycles in 10^{11} cps averaged over 10 sec, is used as the frequency standard. This oscillator is compared against Radio Station WWV at regular intervals, and adjusted as required to maintain an accuracy of the same order as the stability.

The spectrometer sensitivity which was measured by

* This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

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TABLE I. Calculated and observed transitions for Cl^{35} chlorobenzene.

Assignment[a]		Calculated frequency (Mc/sec)	Observed[b] frequency (Mc/sec)	Difference $\nu_c-\nu_0$ (Mc/sec)
$4_{14}\rightarrow 3_{13}$				
	7/2←5/2	10 514.85	...	...
	9/2←7/2	10 515.77	10 515.85	−0.08
	5/2←3/2	10 516.60	...	...
	11/2←9/2	10 517.53	10 517.59	−0.06
$4_{22}\leftarrow 3_{21}$				
	9/2←7/2	11 423.37	11 423.27	+0.10
	7/2←5/2	11 425.87	11 425.88	−0.01
	11/2←9/2	11 430.55	11 430.56	−0.01
	5/2←3/2	11 433.04	...	...
$4_{13}\leftarrow 3_{12}$				
	7/2←5/2	11 882.59	11 882.60	−0.01
	9/2←7/2	11 883.52	11 883.60	−0.08
	5/2←3/2	11 884.35	11 884.22	+0.13
	11/2←9/2	11 885.28	11 885.28	0.00
$5_{15}\leftarrow 4_{14}$				
	9/2←7/2	13 110.88	13 110.90	−0.02
	11/2←9/2	13 111.71	13 111.70	+0.01
	7/2←5/2			
	13/2←11/2	13 112.54	13 112.50	+0.04
$5_{05}\leftarrow 4_{04}$				
	9/2←7/2	13 659.00	13 658.91	+0.09
	13/2←11/2	13 660.23	13 660.23	0.00
$5_{24}\leftarrow 4_{23}$				
	11/2←9/2	14 004.30	14 004.36	−0.06
	9/2←7/2	14 004.81	14 004.85	−0.04
	13/2←11/2	14 007.84	14 007.90	−0.06
	7/2←5/2	14 008.35	14 008.40	−0.05
$5_{23}\leftarrow 4_{22}$				
	11/2←9/2	14 396.70	14 396.64	+0.06
	13/2←11/2	14 400.32	14 400.44	−0.12
$5_{14}\leftarrow 4_{13}$				
	9/2←7/2	14 810.15	14 810.13	+0.02
	11/2←9/2	14 810.97	14 810.98	−0.01
	13/2←11/2	14 811.80	14 811.76	+0.04
$6_{16}\leftarrow 5_{15}$				
	11/2←9/2	15 687.96	15 688.03	−0.07
	13/2←11/2	15 688.51	15 688.53	−0.02
	15/2←13/2	15 689.06	15 689.01	+0.05
$6_{06}\leftarrow 5_{05}$				
	11/2←9/2	16 209.25	16 209.21	+0.04
	15/2←13/2	16 210.07	16 210.05	+0.02
$6_{25}\leftarrow 5_{24}$				
	13/2←11/2	16 768.88	16 768.91	−0.03
	15/2←13/2	16 770.90	16 770.86	+0.04
$6_{24}\leftarrow 5_{23}$				
	13/2←11/2	17 420.86	17 420.94	−0.08
	15/2←13/2	17 422.95	17 423.08	−0.13
$7_{07}\leftarrow 6_{06}$				
	13/2←11/2	18 701.09	18 701.16	−0.07
	17/2←15/2	18 701.67	18 701.58	+0.09
$7_{26}\leftarrow 6_{25}$				
	15/2←13/2	19 512.76	19 512.86	−0.10
	17/2←15/2	19 514.00	19 514.10	−0.10
$7_{25}\leftarrow 6_{24}$				
	15/2←13/2	20 481.48	20 481.49	−0.01
	17/2←15/2	20 482.79	20 482.92	−0.13
$7_{16}\leftarrow 6_{15}$				
	15/2←13/2	20 552.65	20 552.49	+0.16
	17/2←15/2	20 553.16	20 553.13	+0.03
$8_{18}\leftarrow 7_{17}$				
	15/2←13/2	20 785.55	20 785.52	+0.03
	19/2←17/2	20 785.93	20 785.88	+0.05
$8_{08}\leftarrow 7_{07}$				
	15/2←13/2	21 154.80	21 154.72	+0.08
	19/2←17/2	21 155.24	21 155.08	+0.16
$8_{27}\leftarrow 7_{26}$				
	17/2←15/2	22 233.63	22 233.70	−0.07
	19/2←17/2	22 234.49	22 234.45	+0.04
$8_{17}\leftarrow 7_{16}$				
	15/2←13/2	23 344.54	23 344.44	+0.10
	19/2←17/2	23 344.93	23 344.88	+0.05
$8_{26}\leftarrow 7_{25}$				
	17/2←15/2	23 554.13	23 554.17	−0.04
	19/2←17/2	23 554.99	23 555.15	−0.16
$9_{09}\leftarrow 8_{08}$				
	21/2←19/2	23 590.11	23 591.01	−0.10
$9_{37}\leftarrow 8_{36}$				
	19/2←17/2	25 482.33	25 482.31	+0.02
	21/2←19/2	25 483.66	25 483.55	+0.11
$9_{36}\leftarrow 8_{35}$				
	19/2←17/2	25 810.41	25 810.45	−0.04
	21/2←19/2	25 811.80	25 811.75	+0.05
$9_{18}\leftarrow 8_{17}$				
	21/2←19/2	26 068.30	26 068.26	+0.04
$10_{1,10}\leftarrow 9_{1,9}$				
	23/2←21/2	25 817.83	25 817.72	+0.11
$10_{0,10}\leftarrow 9_{0,9}$				
	23/2←21/2	26 022.97	26 022.89	+0.08
$10_{2,9}\leftarrow 9_{2,8}$				
	23/2←21/2	27 598.48	27 598.90*	+0.42
$10_{8,8}\leftarrow 9_{8,7}$				
	21/2←19/2	28 312.04	28 312.94	+0.10
	23/2←21/2	28 314.00	28 313.87	+0.13
$10_{37}\leftarrow 9_{36}$				
	21/2←19/2	28 846.34	28 846.35	−0.01
	23/2←21/2	28 847.37	28 847.45	−0.08
$10_{28}\leftarrow 9_{27}$				
	21/2←19/2	29 639.34	29 639.41	−0.07
	23/2←21/2	29 639.74	29 639.73	+0.01
$11_{1,11}\leftarrow 10_{1,10}$				
	25/2←23/2	28 315.36	28 315.21	+0.15
$11_{0,11}\leftarrow 10_{0,10}$				
	25/2←23/2	28 459.22	28 459.03	+0.19

[a] Where component transitions $F'\leftarrow F$ are unresolved, only the largest value of $F'\leftarrow F$ is given.
[b] Frequencies ±0.10 Mc/sec except those noted (*), which are ±0.3 Mc/sec.

TABLE II. Calculated and observed transitions for Cl^{37} chlorobenzene.

Transition[a]		Calculated frequency (Mc/sec)	Observed[b] frequency (Mc/sec)	Difference $\nu_c-\nu_0$ (Mc/sec)
$5_{15}\leftarrow4_{14}$				
	9/2←7/2	12 806.03	12 806.03	0.00
	11/2←9/2	12 806.68	12 806.63	+0.05
	13/2←11/2	12 807.33	12 807.31	+0.02
$5_{05}\leftarrow4_{04}$				
	9/2←7/2	13 342.36	13 342.34	+0.02
	13/2←11/2	13 343.33	13 343.31	+0.02
$5_{24}\leftarrow4_{23}$				
	11/2←9/2	13 654.04	13 654.09	−0.05
	13/2←11/2	13 656.83	13 656.80	+0.03
$5_{23}\leftarrow4_{22}$				
	13/2←11/2	14 010.49	14 010.45	+0.04
$5_{14}\leftarrow4_{13}$				
	9/2←7/2	14 423.37	14 423.35	+0.02
	11/2←9/2	14 424.02	14 424.01	+0.01
	13/2←11/2	14 424.67	14 424.62	+0.05
$7_{07}\leftarrow6_{06}$				
	17/2←15/2	18 289.89	18 289.90	−0.01
$7_{26}\leftarrow6_{25}$				
	15/2←13/2	19 031.69	19 031.28*	+0.41
	17/2←15/2	19 032.67	19 032.36*	+0.31
$7_{25}\leftarrow6_{24}$				
	15/2←13/2	19 915.02	19 914.94	+0.08
	17/2←15/2	19 916.06	19 915.98	+0.08
$7_{16}\leftarrow6_{15}$				
	17/2←15/2	20 032.05	20 032.03	+0.02
$8_{18}\leftarrow7_{17}$				
	19/2←17/2	20 314.43	20 314.31	+0.12
$8_{08}\leftarrow7_{07}$				
	15/2←13/2	20 695.72	20 695.94*	−0.22
	19/2←17/2	20 696.05	20 696.39*	−0.34
$8_{27}\leftarrow7_{26}$				
	17/2←15/2	21 690.47	21 690.38	+0.09
	19/2←17/2	21 691.12	21 690.99	+0.13
$8_{25}\leftarrow7_{24}$				
	17/2←15/2	22 219.37	22 219.05	+0.32
	19/2←17/2	22 220.90	22 220.56	+0.34
$8_{17}\leftarrow7_{16}$				
	19/2←17/2	22 765.90	22 765.88	+0.02
$8_{26}\leftarrow7_{25}$				
	17/2←15/2	22 903.08	22 902.90	+0.18
	19/2←17/2	22 903.82	22 903.67	+0.15
$9_{19}\leftarrow8_{18}$				
	21/2←19/2	22 783.97	22 783.89	+0.08
$9_{09}\leftarrow8_{08}$				
	21/2←19/2	23 081.53	23 081.53	0.00
$9_{28}\leftarrow8_{27}$				
	21/2←19/2	24 326.62	24 326.60	+0.02
$9_{36}\leftarrow8_{35}$				
	19/2←17/2	25 110.26	25 110.19	+0.07
	21/2←19/2	25 111.35	25 111.32	+0.03
$9_{18}\leftarrow8_{17}$				
	21/2←19/2	25 439.13	25 438.97	+0.16
$9_{27}\leftarrow8_{26}$				
	21/2←19/2	25 884.57	25 884.80*	−0.23
$10_{1,10}\leftarrow9_{19}$				
	23/2←21/2	25 240.12	25 240.10	+0.02
$10_{0,10}\leftarrow9_{0,9}$				
	23/2←21/2	25 461.18	25 461.17	+0.01
$10_{28}\leftarrow9_{37}$				
	21/2←19/2	27 590.94	27 590.67	+0.27
	23/2←21/2	27 591.70	27 591.30	+0.40
$10_{19}\leftarrow9_{18}$				
	23/2←21/2	28 042.49	28 042.16	+0.33
$10_{37}\leftarrow9_{36}$				
	21/2←19/2	28 049.72	28 049.41	+0.31
	23/2←21/2	28 050.52	28 050.18	+0.34
$11_{1,11}\leftarrow10_{1,10}$				
	25/2←23/2	27 684.98	27 684.90	+0.08
$11_{0,11}\leftarrow10_{0,10}$				
	25/2←23/2	27 843.18	27 842.95	+0.23

[a] Where component transitions $F'\leftarrow F$ are unresolved, only the largest value of $F\leftarrow F$ is given.
[b] Frequencies ±0.10 Mc/sec except those noted (*), which are ±0.3 Mc/sec.

observing the $O^{16}C^{12}S^{33}$, $J=1\rightarrow2$, $F=\frac{3}{2}\rightarrow\frac{1}{2}$ transition at 24 032.75 Mc/sec is about $(\alpha_g)=0.5\times10^{-8}$ cm^{-1}, with a gas pressure of about 1μ in a 6-ft stark cell at −80°C. The S/N ratio was about 2/1 on an oscilloscope with a time constant of 0.1 sec. Most of the observed absorption lines are considerably stronger than this.

The chlorobenzene which was a CP-grade sample manufactured by Eastman Organic Chemicals was vacuum distilled and used without further purification.

3. OBSERVED SPECTRUM

The chlorobenzene spectrum was observed between 8 to 30 Gc/sec, both on an oscilloscope and on a recorder. The low J transitions were quite weak and could be seen only with the recorder. A study of the recorder traces of suitable low J transitions ($J=3\rightarrow4$ and $J=4\rightarrow5$) was used for the analysis of the quadrupolar fine structure. The coupling constants obtained from this analysis were used to recompute the expected splittings for the remaining transitions. In general, most of the higher J transitions were split into doublets, each member of which consisted of two unresolved quadrupolar transitions. The splitting of these doublets closely fits the theoretical values obtained from the coupling constants of the low J transitions. The computed quadrupolar frequency shifts were subtracted from the observed frequencies in order to arrive at a set of "pure" rotational frequencies which were then used

to compute a refined set of rotational constants. A new set of frequencies was then computed and compared to the observed frequencies. The frequencies were computed with the aid of an IBM 7090 program obtained from Beaudet.[15] The resulting assignment for the two isotopic chlorobenzenes is given in Tables I and II, for a representative set of lines. The difference between the calculated and observed frequencies is also given. An inspection of these tables shows that the frequency differences are quite small which is in agreement with a rigid molecular model. The slightly larger deviations observed for Cl^{37} chlorobenzene are attributed to experimental errors in the frequency measurements, and not to centrifugal distortion effects.

A fair number of lines were observed in addition to those which were assigned. Many of these lines belong to molecules in excited vibrational states, as judged from their temperature dependence. However, no attempt was made to assign these lines at this time. In addition, several weak high J lines were also observed and appear to belong to one of the C^{13} isotopic chlorobenzenes. Further work on the C^{13} isotopic molecules is in progress.

4. QUADRUPOLE COUPLING CONSTANTS

The quadrupolar coupling constants were initially determined by fitting the $\Delta F=+1$ components of the $J=4\rightarrow5$ transitions, $J=4_{14}\rightarrow5_{15}$, $J=4_{13}\rightarrow5_{14}$, $J=4_{23}\rightarrow5_{24}$, $J=4_{22}\rightarrow5_{23}$. However, only one of these transitions was completely resolved into all four of its $\Delta F=+1$ components. The two $K_{-1}=1$ transitions were split into triplets with the weak $F=\frac{5}{2}\rightarrow\frac{7}{2}$ component unresolved from the stronger $F=\frac{3}{2}\rightarrow\frac{1}{2}$ component in both cases. The theoretical splitting for these lines is about 0.06 Mc/sec. The resulting quadrupole coupling constants are given in Table III.

In spite of the magnitude of the rotational asymmetry parameter, $\kappa=-0.85$, in chlorobenzene, an estimate of the quadrupolar asymmetry parameter η could not be obtained because the quadrupolar splittings are insensitive to variations in η for a C–Cl bond located on the molecular principal axis of symmetry. The ratio of the observed coupling constants, $eqQ(Cl^{35})/eqQ(Cl^{37})=1.268\pm0.005$, is in very good agreement with the ratio of the nuclear quadrupole moments[16] $Q(Cl^{35})/Q(Cl^{37})=1.2688$.

The quadrupolar coupling constants for chlorobenzene in the gas phase are larger than the constants found in the solid state, where $eqQ(Cl^{35})=-69.244$ Mc/sec.[4,5] However, the change in the quadrupolar coupling constant in chlorobenzene on going from the gaseous to the solid state is smaller than the corresponding change for methyl chloride.[4,5] Furthermore, the coupling constants found in chlorobenzene in both physical states are intermediate between those found for methyl chloride in the corresponding states.[17] This would indicate that there is a smaller change in the ionic character of the C–Cl bond in chlorobenzene than there is in methyl chloride on changing state. In the gas phase, the ionic character decreases, thereby raising the coupling constant.

TABLE III. Summary of observed rotational and quadrupolar constants for chlorobenzene.[a]

Cl^{35} chlorobenzene	Cl^{37} chlorobenzene
$A=5672.95$ Mc/sec	$A=5672.53$ Mc/sec
$B=1576.774$ Mc/sec	$B=1532.790$ Mc/sec
$C=1233.672$ Mc/sec	$C=1206.571$ Mc/sec
$I_A=89.113$ amu-Å^2	$I_A=89.119$ amu-Å^2
$I_B=320.6109$ amu-Å^2	$I_B=329.8110$ amu-Å^2
$I_C=409.7775$ amu-Å^2	$I_C=418.9816$ amu-Å^2
$\kappa=-0.845424$	$\kappa=-0.853908$
$b=-4.01943\times10^{-2}$	$b=-3.79073\times10^{-2}$
$\Delta=0.054$ amu-Å^2	$\Delta=0.052$ amu-Å^2
$eqQ=-71.10\pm0.50$ Mc/sec	$eqQ=-56.10\pm0.50$ Mc/sec

[a] Conversion factor: 505 531 (Mc/sec)(amu-Å^2).

A comparison of the value of the quadrupolar coupling constant in the gas phase to the values of the corresponding coupling constants for the polychlorinated benzenes in the solid state shows that the increased eqQ value of the gas phase is almost equivalent to the increase which is obtained by the addition of an *ortho* chlorine atom to chlorobenzene in the solid state.[5]

5. ROTATIONAL CONSTANTS AND MOLECULAR STRUCTURE

The rotational and quadrupolar constants for the two chlorine isotopic forms of chlorobenzene are given in Table III, along with the inertial defect, Δ. The observed rotational lines are accurately described by a rigid rotor analysis without the inclusion of centrifugal distortion corrections. The small value of such centrifugal distortion is to be expected in a molecule as heavy as chlorobenzene. For a planar chlorobenzene model, the inertial defect would also be expected to be small, which is in accordance with observation. The observed inertial defect is intermediate between the inertial defects which have been observed for fluorobenzene[9] and benzonitrile.[10,11]

With only two isotopic molecular species of chlorobenzene, a complete structure determination is not possible. However, an estimate of the C–Cl bond distance can be made on the basis of suitable simplifying assumptions. If a regular hexagonal ring and a C–H

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bond distance of 1.084 Å are assumed, then the C–C distance can be calculated from the A moment of inertia as 1.399 Å. With these values for the C–H and C–C bond distances, the B moment of inertia may be used to determine the chlorine coordinate, from which a C–Cl distance of 1.712 Å is obtained. Another estimate of the C–Cl bond distance may be made by assuming that the benzene ring structure is the same as that found in benzonitrile,[11] an assumption which may not be warranted. With this assumption the C–Cl bond length is 1.730 Å. The true value for this bond length probably lies somewhere between these values, which may be taken as limits. The C–C distance obtained from the chlorobenzene A moment of inertia is in very good agreement with the value of this bond length which was observed by Stoicheff[18] in the Raman analysis of benzene.

6. DIPOLE MOMENT

The dipole moment was measured from the Stark effect of two different transitions, the $J_{K_{-1}K_{+1}}=3_{21}\rightarrow 4_{22}$, $F=\frac{5}{2}\rightarrow\frac{7}{2}(M=0)$ and the $J_{K_{-1}K_{+1}}=3_{12}\rightarrow 4_{13}$, $F=\frac{9}{2}\rightarrow\frac{11}{2}$ $(M=1)$. Some difficulty was experienced in obtaining transitions which were reasonably clear of interfering Stark lobes from neighboring transitions. These two transitions appeared to be about the best available considering both the interference and the very weak absorption coefficients of these low J lines. All measurements were made for strong field conditions ($V>600$ V/cm) in order to avoid complication in interpreting a superposition of intermediate field patterns from adjacent lines. The experimental precision on the individual measurements was ±6%. The Stark cell electric field was calibrated by measuring the Stark shift for OCS at the same input square-wave voltages and at the same waveguide temperature (slightly above dry-ice temperature) immediately before and after the measurements were made on chlorobenzene. The dipole moment, which is directed along the I_a axis, is 1.782±0.06 D, in good agreement with the value determined by classical methods.[19]

7. DISCUSSION

Both the dipole moment and the C–Cl bond distance can be used to estimate the fractional double-bond character of the C–Cl bond. If the C–Cl bond distance in methyl chloride is taken as representative of a pure single bond, then the C–Cl shortening in chlorobenzene is about 0.07 Å, which corresponds to about 15% double-bond character, the same as was originally obtained by Pauling.[20] On the other hand, the double-bond character as estimated from the dipole moment[19] is increased by a very small amount, to 4%, which is still too small to remove the discrepancy between the two methods of estimating double-bond character.[21] Unfortunately, the C–Cl bond in chlorobenzene is located on the axis of the A moment of inertia, and, therefore, it is not possible in this study to determine the quadrupolar parameter η, which is also a measure of the double-bond character, in hope of determining which, if either, of these two values for the double-bond character is correct.

With the lack of adequate data on the other isotopic species of chlorobenzene, it would be premature to attempt a detailed comparison of the substituted benzenes which have been studied. However, a trend has been noticed which may or may not be real. The A moments of inertia for all of the substituted benzenes in which atom substitution occurs on the A axis should be essentially constant. That they are not could arise from either inertial defects or from a real although small difference in the benzene ring structure. The present results for chlorobenzene, and the reported results for fluorobenzene are both insufficient to resolve this observation.

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